DERMAL AND URINARY MONITORING OF NECTARINE HARVESTERS EXPOSED TO AZINPHOS-METHYL RESIDUES IN FRESNO COUNTY CALIFORNIA 1988

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SUMMARY

During July of 1988, a study of dermal exposure and biological monitoring of 26 workers harvesting nectarines in an azinphos-methyl treated orchard was conducted in Fresno County. Guthion[R] 50W was applied to an orchard 52 days prior to the study. The rate was 0.7 lb active ingredient per acre in 20 gallons of water. The dermal samples were analyzed for the presence of azinphos-methyl and azinphos-methyl oxon. The orchard foliage was also monitored for dislodgeable foliar residues of azinphos-methyl and its oxon. Average dislodgeable residues for the study period were 0.31 ug/cm^2 and 0.008 ug/cm^2 for azinphos-methyl and the oxon.

The dermal monitoring was conducted on three of four picking days and consisted of a long sleeved 100% cotton knit undershirt, a combined face and neck wipe, and a handwash sample. Dermal samples were collected at the end of the 8-hour work period. The mean of the potential dermal exposure for the three days monitored was 17.2 ± 5.7 mg per day. The undershirt accounted for over 90% of the exposure. A transfer factor of 6935 cm^2/hr was calculated, using hourly mean potential exposure of 2150 ug/hr divided by the mean foliar dislodgeable residue of 0.31 ug/cm^2.

The urinary monitoring consisted of 24-hour composite voids over 7 consecutive days. Sample aliquots were analyzed for the presence of dialkyl phosphates and creatinine concentration. Mean dimethyl thiophosphate excretion was 0.49 ± 0.19 mg. Using data from human and animal dermal .PN2

absorption studies a dermal exposure was estimated and found to be ~5 ± 2 mg.

Results of blood draws taken from 18 workers showed no physiological response to the workers' exposure in the lowering of either plasma or red blood cell cholinesterase levels.

INTRODUCTION

Monitoring workers exposure to a pesticide during harvest activities provides information which is used in a risk assessment analysis. This analysis determines if the pesticide has a significant margin of safety. In the past, worker exposure studies have included the dermal monitoring of workers by using gauze pad or shirt dosimetry techniques (Durham and Wolfe, 1962; Spencer et al., 1989) including biological monitoring of urine and/or blood for metabolites (Ritter and Franklin, 1989). Biological monitoring yields the most useful data when the pharmacokinetic information is known about the percutaneous transport and the urinary metabolite elimination of pesticides in rats, mice, or, ideally, in humans. If this latter information is known, it may be possible to accurately assess the level of exposure (via biological monitoring) experienced by workers to a pesticide.

This paper characterizes the level of exposure nectarine harvesters have to azinphos-methyl (O,O-Dimethyl S-[4-oxo-1,2,3-benzotriazin-3(4H)-yl methyl] phosphorodithioate). Initial worker exposure investigations were driven by the observation that field workers in California were being poisoned by exposure to organophosphates (Maddy, 1975 and CDFA, 1967). Azinphos-methyl is a highly toxic organophosphate insecticide and cholinesterase inhibitor widely used to control certain insects on stone fruits. However, it has been implicated as the cause of field worker illnesses (Maddy et al., 1981). Cholinesterase inhibiting pesticides may pose a potential hazard to field workers who enter a treated area because they have significant contact with treated plants and soils (Maddy et al., 1987). Azinphos-methyl (Guthion^R) is a suitable candidate for an exposure assessment study. Biological monitoring was chosen as there is: 1) background information on the dermal absorption in humans and laboratory animals (Feldmann and Maibach, 1974; Franklin et al., 1986; Ritter and Franklin, 1989) and 2) related field studies of mixer/loader/applicators and harvesters (Franklin et al., 1981; Popendorf et al., 1979) and apple thinners (Davis et al., 1983). Examining applicators' exposure to azinphos-methyl is justified as they are at greater risk than harvesters of being exposed to higher pesticide concentrations. Many organophosphate pesticides undergo a conversion from -thions to -oxons and may be more toxic than the parent compound (Morgan, 1982). For example, azinphos-methyl oxon has a dermal toxicity of approximately thirty times the parent compound (Knaak et al., 1980). These degradation products may be present in greater concentration at harvest than at the time of application. This may increase potential hazard to harvesters and result in a depression of cholinesterase blood levels. Levels of pesticides to which harvesters are exposed are lower compared to the applicators, however, dermal absorption of pesticide residues for harvesters may be greater due to increased plant residue/pesticide/worker interactions.

In this study, nectarine harvesters wore long-sleeved (cotton) undershirts while being monitored for dermal exposure to azinphos-methyl. Hand washes and face/neck wipes were also collected. Twenty-four hour composite urine voids were collected, blood samples were drawn for determination of plasma and RBC cholinesterase levels and dislodgeable foliage residue samples were collected. Dermal dosimetry and urinary excretion data was used to estimate the exposure of the nectarine harvesters. The relationship between foliage residues and dermal exposure was also evaluated.

In order to assess the hazard to field workers who enter treated fields, the amount of pesticide available for absorption must be accurately measured. Guidelines for measuring exposure to agricultural applicators using dermal dosimeters and biological monitoring have been developed by the Environmental Protection Agency, 1987; Mull and McCarthy for the National Agricultural Chemical Association, 1986; and the World Health Organization, 1982. Popendorf and Leffingwell, 1982, Nigg and Stamper, 1984, and Zwieg, 1985, have developed empirical ratios of dislodgeable foliage residues and dermal pesticide exposure by using units of leaf area contacted/time as an indication of residue transferability.

MATERIALS AND METHODS

Cooperation in conducting this study was obtained from a packing company in Fresno County, California in May of 1988. The azinphos-methyl treated nectarine (Del Rio Rey variety) orchard used in this study was provided by the packing company. The field of 9.5 acres was planted in hedgerows running north-south. The trees were spaced four feet apart and were pruned on two main scaffolds at a height of 12 feet. The packing company provided a Spanish speaking crew of 28 workers for the dermal and biological monitoring. A Spanish speaking interpreter explained the study procedures and asked for their voluntary cooperation. The all-male crew ranged in ages from 17 to 46 years with half the crew under 25 years. Over 50% of the crew had worked for the packing company between five to fifteen years. Their normal work attire consisted of long sleeved shirts/long pants, socks/shoes and some wore hats. The crew had not yet worked in any organophosphate-treated orchards this 1988 season. The method and number of workers monitored each day during the study is shown in the following schedule:

Table I

	Study schedule						
Days post-application	52	53	54	55	56	57	58
	Number of workers						
	PK		PK		PK	PK	
Potential dermal exposure	6a/	0	13	0	12	0	0
Urinary alkyl phosphates	6	6b/	20c/	18d/	14	14	14

PK picking days

a/ The first 6 workers were monitored by both methods.

b/ Days 53, 55 and 58 were follow-up days for urinary metabolite monitoring.

c/ Twenty includes 14 from the second picking day and 6 from the first picking also being monitored dermally on picking day 2.

d/ Two workers did not provide samples for follow-up day 55.

The field was treated once with azinphos-methyl 52 days before the first picking at 0.7 pound active ingredient per acre in 20 gallons of water. The soluble powder formulation (35% a. i.) used was Guthion® 35, (Mobay) EPA# 3125-379. No other organophosphates were applied to the orchard during this season. The orchard was sampled for dislodgeable foliar residues using the method of Gunther et al., (1973). Samples were taken prior to the application on post-application days 1, 2, 6, 7, 14, 21, 28, 35, 42, 49, 84 and during four picking days (52, 54, 56 and 57). One sample consists of forty leaf disks (2.54 centimeters in diameter), cut with a Birkestrand leaf punch. Five random samples, each collected from forty trees, were taken in the field at a height of five feet. Sample jars were sealed with aluminum foil, capped, and stored on ice until analysis.

The degradation of azinphos-methyl was plotted against time and an average half-life was calculated using the first-order exponential decay model:

$$Y = B_o + B_1 * \log_{10}(R)$$

where $Y = \log_{10}$ of residue at any time t

where B_o = initial deposition in ug/cm^2

B_1 = first order rate constant in $ug/cm^2/time$

and R = mean residue at each sampling interval in ug/cm^2

The equation to determine the estimate of half-life is:

$$t_{1/2} = \log_{10}(1/2)/B_1$$

where t = time in days

A new Health Knit brand 100% cotton knit (long-sleeved white) undershirt was issued to the participants at the beginning of each monitoring day. Shirts were worn the entire work day (0630 to 1430 hours). Due to extreme high temperatures (over 105°F) nothing was worn over or under the provided undershirt. At the end of the work day the workers' shirts were removed and placed into sealed plastic bags. The workers then washed both hands for two minutes in 500 mL of 1% sodium dioctyl sulfosuccinate contained in one-gallon plastic bags. Workers were then given two pre-moistened disposeable wipes (Chubs® brand) to wipe their face and neck. The handwashes were poured into Nalgene® bottles and the wipes were stored in four-ounce glass jars. All dermal exposure samples were stored on dry ice until analysis.

All crew members provided a pre-exposure urine sample. Each crew member participating in urinary metabolite monitoring was provided with three (one-liter polyethylene) bottles for urine collection daily. They were instructed to void into the bottles for a 24-hour period. Additional new bottles were given to them the following day. At every 24-hours the sub-samples for each individual were mixed in two, 2-liter containers, by pouring back and forth five times. Total volume was recorded and an aliquot (100 mL) was decanted into a 250-mL polyethylene bottle which was stored on dry ice and shipped to the laboratory.

On day 5 of the study (56 days post-application) blood samples were drawn from 18 workers and were sent to Roche Biomedical Laboratories. Analysis of red blood cell and plasma cholinesterase levels were requested. Two weeks after completing the study blood draws and analyses were repeated. The blood samples were analyzed using the Ellman method (1961).

Dislodgeable residue leaf samples were prepared according to Gunther et al., (1973). Samples were shaken three times with water containing a few drops of a sodium dioctyl sulfosuccinate solution). The aqueous "strip" was saturated with sodium chloride and extracted with ethyl acetate (2 X 50 ml) Anhydrous Na_2SO_4 was added to the combined extracts to remove dissolved water. After volume reduction the samples were analyzed by gas liquid chromatography. Dermal dosimeters were analyzed by tumbling the clothing or wipes with ethyl acetate. Handwashes were extracted using ethyl acetate. The extracts were dried with anyhydrous sodium sulfate and diluted as necessary for analysis. Chromatography was done on a Hewlett-Packard 5880A chromatograph equipped with a nitrogen-phosphorous detector. The chromatographic conditions were: column, 10m x 0.52mm HP 50% phenyl methyl silicone; carrier gas (He), 20 mL/min; H_2, 2 mL/min; air, 90 mL/min; injector temperature, 275° C; oven temperature, 235° C isothermal. The retention time of azinphos-methyl, using the above conditions, was 6.49 minutes and the retention time of azinphos-methyl OA was 5.32 minutes. Minimum detectable levels (in micrograms per sample) were: 120 for undershirts, 0.2 for wipes, 1.0 for handwashes and 0.5 for dislodgeable foliar residues.

Alkyl phosphates were determined as reported by Weisskopf and Seiber (1987) with the following modifications in the extraction technique. After the urine sample was passed through the cyclohexy extraction cartridge, the cartridge was washed with 2 ml hexane followed by aspriation at a vacuum of 3 in. Hg for 3 minutes. The dialkyl phosphates were eluted from the cartridge with acetone to 3 ml of eluate. Chromatography was done on a Varian 6000 gas chromatograph equipped with a flame photometric detector. The chromatographic conditions were: column, 15m x 0.5mm DB 1701 (J&W Scientific); carrier gas (He), 4.5mL/min; H_2, 150 mL/min; air #1, 80mL/min; air #2, 170mL/min; make-up gas (He), 50mL/min; injector temperature, 300° C; and column temperature, 110° C isothermal. The minimum detectable level is 0.1 ng or is 35 ppb in urine. The analytical method can determine only the sulfur containing dialkyl phosphates.

The determination of creatinine levels was conducted by Roche Biomedical Laboratories.

RESULTS

Foliar dislodgeable residues were taken over twelve weeks following the application. A log/linear regression was performed on the residue data and is plotted in Figure 1 (r=-0.94). The half-life of azinphos-methyl residue was calculated to be 30 days. Foliage sample results taken daily when workers harvested in the treated field are reported in Table II. The samples were analyzed for azinphos-methyl and its oxon. The mean of azinphos-methyl and its oxon residue was 0.31 ± 0.03 ug/cm^2 for the four harvest days.

Potential dermal exposure measurements of azinphos-methyl residues are reported in Table III. The mean for the three days of monitoring was 17.2 ± 5.7 milligrams (mg). Appendix I contains the data used to calculate the potential dermal exposure, which includes residues of azinphos-methyl and its oxon. The undershirt (arm and torso exposure) accounted for over 90% of the exposure measured. Undershirt data ranged from 5.7 to 31.8 mg/shirt with a mean of 15.6 ± 5.5 mg. Handwash data ranged from 0.3 to 3.4 mg/sample with a mean of 1.45 ± 0.83 mg. Facewipes ranged from 0.025 to

0.199 mg/sample with a mean of 0.091 ± 0.040 mg.

Cholinesterase activity results for workers participating in both the blood draws are shown in Appendix II. Analysis using a paired t-test showed no significant difference ($p > 0.05$) between their initial and follow-up values for either plasma or RBC. Table IV reports the group means and standard deviation of dimethyl thiophosphate (DMTP) excreted in 24 hours and azinphos-methyl equivalents from the urinary metabolite monitoring. Appendix 3 reports the individual twenty-four hour urinary metabolite monitoring, including creatinine levels and azinphos-methyl equivalents. The only metabolite of azinphos-methyl that was detected in any of the urine samples was DMTP. A ratio of the molecular weight of azinphos-methyl to the molecular weight of DMTP was employed to calculate the urinary results to an absorbed dose of azinphos-methyl equivalents.

DISCUSSION

The hands contributed 8.4% to the potential dermal exposure and the face-neck area, 0.5%. More than 90% of the measured potential dermal exposure to azinphos-methyl residues was found on the long-sleeved shirt. Handwipes were followed by handwashes on the first day of the study. Since the workers' hands were noticeably dirty after using the wipes, handwashes alone were employed on all other study days. However, analysis of the data found the wipes removed 77 ± 8% of the total residue on the hands (see Appendix 1). The high percentage of residues found demonstrates the effectiveness of handwipes in removing azinphos-methyl residues. This appears to be an appropriate method for measuring exposure to the face and neck regions, an area almost impossible to monitor using standard patch techniques.

All pre-exposure urine samples were negative for the presence of alkyl phosphates. Since the crew had not worked in any organophosphate-treated field previous to this study, all DMTP found in the urine samples can be assumed to be due to the exposure while working in the treated orchard. For days 1-2 (52-53) and days 3-4 (54-55) of the study, azinphos-methyl equivalents are present in urine at equal concentration. Day 5 and 6 (56-57) seem to show accumulative effects of the previous days' exposure. Day 7, a non-exposure day, had the lowest mean of the study.

Exposure influenced urine results as follows: when an exposure day (days 1, 3) was followed by a day of non-exposure (days 2, 4), all urine results were attributed to the day of exposure. This gave three comparable groups of urinary data each composed of a 48-hour urine collection (Table IV). For a fourth group, day 5 was an exposure day and day 6 consisted of 4-hours exposure in the treated field. The workers then harvested in an untreated field for 4 more hours. The residues transferred to their clothing from the treated field were an exposure source for the remainder of the workday. Recent work suggests that a residue loading effect exists with dermal dosimetry media exhibiting a greater absorptive capacity during the initial portion of the exposure (Fenske, 1989). Metabolite excretion for days 5-7 was thus assumed due to similar exposures on days 5 and 6.

Data developed by Feldmann and Maibach (1973), determined the percutaneous penetration of several pesticides in man using radiolabeled ^{14}C pesticides. They determined that 15.9% of a dermal azinphos-methyl dose would be excreted in the urine over four days with approximately 11% excreted in the first 48 hours. Franklin et al., (1986) and (1982) found a similar ratio (10:1) between humans and rats of applied dose of azinphos-methyl to DMTP excreted in the first 48 hours. Exposure estimates in the present study can be derived from metabolite data and compared to the observed potential dermal exposure (Table V).

Spear et al., (1977), and Popendorf et al., (1979), found 25-47% of residues deposited outside clothing reached the skin. In this study the predicted exposure from DMTP metabolite monitoring is 29 $\pm$ 15% of the observed potential exposure.

Data from ten subjects evaluated by both dermal and urinary monitoring had no significant relationship between metabolite excretion and dermal exposure. Adjusting metabolite output (DMTP) or azinphos-methyl equivalents for an average creatinine output of 1500 mg per day did not improve the relationship. The inability to relate these two exposure components emphasizes the variation in 24-hour voids collected under field work conditions. Average creatinine results for these 10 subjects were 1220 $\pm$ 653 mg (n=20) and, for all workers, 1077 $\pm$ 507 mg (n=92). The CV for both groups approaches 50%. If worker weights are calculated from these data using an average creatinine excretion of 23.5 mg/kg (Bingham and Cummings, 1985), a worker in this study would weigh between 24 and 78 kg. Average daily urine volumes for the 10 subjects were 1.0 $\pm$ 0.5 L and, for all workers, 0.8 $\pm$ 0.4 L, again giving a CV of 50%. If these collections represent complete daily voids, then the lower flow rates (0.3 mL/min) represent an abnormal state (Greenberg and Levine, 1989).

The dislodgeable foliar residue was constant with a mean of 0.31 ug/cm^2. The dislodgeable residues found at the 14-day reentry (0.85 ug/cm^2) are similar to residues from other studies with similar rates of active ingredient (a.i.) per acre; 0.88 ug/cm^2 and 0.85 at 1 lb a.i./100 gallons, Maddy et al., (1984), Maddy et al., (1986), respectively, and 0.81 ug/cm^2 at 0.53 lb a.i./250 gallons by Spencer et al., (1989). Maddy et al., (1982), found residue levels averaged 0.12 ug/cm^2 at 14 days, at 2 lb a.i./A, with five times the dilution (500 gpa).

Popendorf et al., (1982), Nigg et al., (1984), and Zweig, et al. (1983 and 1985), developed a model for calculating a transfer factor for leaf surface area contacted per hour. The calculation of a transfer factor can be made from this study using the hourly mean potential exposure of 2150 ug and the mean dislodgeable residue of 0.31 ug/cm^2 (2150 ug/hr divided by 0.31 ug/cm^2 = 6935 cm^2/hr). This transfer factor can be used to calculate a potential dermal exposure at any point in time on the decay curve or from a known dislodgeable residue. Using this transfer factor a potential dermal exposure estimated at the 14-day reentry interval would be 47.4 mg per day. This is about 3 times the exposure found during the harvest period. Davis et al., (1983), and Popendorf et al., (1979), conducted studies on worker exposure to azinphos-methyl residues in apples and peaches, respectively. They found dermal exposures of 3.3 mg/hr in apples and 1.7 mg/hr in peaches at corresponding dislodgeable foliar levels of 1.6 and 0.4 ug/cm^2. Transfer factors calculated from these studies would be 2078 and 4250 cm^2/hr for the Davis and Popendorf studies, respectively.

CONCLUSIONS

Data in this study indicate a one-day exposure to azinphos-methyl residues on treated foliage can result in a determinable level of urinary metabolite excretion. The study also indicates that workers do not manifest lowered levels of red blood cell or plasma cholinesterase levels in response to 3-4 days of working in azinphos-methyl treated fields with DFR levels of 0.31 ug/cm^2. To more fully characterize azinphos-methyl residues' behavior and their fate in the body, future exposure studies should include the collection of complete urine samples until no metabolites are detected. Future studies might be directed at determining the differences in dermal exposures and dermal dose estimates as measured by a single layer of clothing compared to a dosimetry shirt worn beneath normal working attire. This would require that weather conditions permitted the wearing of multiple layers of clothing.

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Table II

Azinphos-methyl Dislodgeable Foliar Residues

Post Application Day	PK	AM/oxon	N	Mean (ug/cm^2)	SD	Median	Range	Temperature °F High	Low
52	1	AM	30	0.27	0.09	0.28	0.13 - 0.44	105	70
		Oxon	30	0.007	0.004	0.006	0.003- 0.017		
54	2	AM	12	0.33	0.07	0.33	0.25 - 0.46	112	76
		Oxon	12	0.008	0.003	0.008	0.003- 0.013		
56	3	AM	6	0.31	0.06	0.32	0.21 - 0.38	108	75
		Oxon	6	0.008	0.008	0.007	0.007- 0.011		
57	4	AM	6	0.31	0.06	0.30	0.22 - 0.40	105	73
		Oxon	6	0.008	0.002	0.009	0.005- 0.014		

PK = picking day

Table III

Azinphos-Methyl Potential Dermal Exposure of Nectarine Pickers

Post Application Day	N	Avg (milligrams/day*)	SD	Median	Minimum	Maximum	Daily Transfer** Factor cm^2/hr
52	6	12.5	1.9	12.8	9.7	14.6	5641
54	13	17.4	4.3	18.8	6.7	21.7	6435
56	12	19.3	7.0	19.4	6.4	34.2	7586
Total	31	17.2	5.7	18.0			

*milligrams/day includes azinphos-methyl parent and oxon.
**Daily transfer factor calculated by dividing hourly average potential exposure by the mean daily dislodgeable residue (see Table I).

Table IV

Urinary Excretion and Potential Dermal Exposure of Nectarine Pickers to Azinphos-Methyl

Post Application Day	PK	N	DMTP mg/24 Hour Mean	DMTP mg/24 Hour SD	AM Equivalents Corrected for Creatinine Mean	AM Equivalents Corrected for Creatinine SD	AM (mg) Dermal Exposure Potential Mean	SD	N	Hours Exposed
52[1]	*	6	0.35	0.40	0.83	0.91	12.5	1.9	6	8
53		6	0.23	0.22	0.83	1.14				0
54	*	6	0.22	0.17	0.60	0.36	19.7	2.5	4	8
55		6	0.12	0.07	0.60	0.18				0
54[2]	*	13	0.13	0.21	0.37	0.49	17.4	4.3	13	8
55		14	0.13	0.08	0.28	0.19				0
56	*	14	0.52	0.47	1.38	1.09	19.4	7.0	12	8
57	*	14	0.62	0.43	1.52	0.82				4
58		14	0.12	0.10	0.34	0.22				0

PK=picking day

1 Ten workers in group 1 (days 52,53,54 and 55) contributing both dermal exposure using long sleeve undershirts and 24 hour voids.

2 Two separate groups of workers; one group gave 24 hour urine samples and the second group was monitored for dermal exposure.

Equivalents are calculated from the ratio of azinphos-methyl (AM) to dimethylphosphorothioate (DMTP) times actual DMTP found.

example: mol. wt. of AM (317)/mol. wt. of DMTP (142) = 2.23 x DMTP found
2.23 x 349 ug DMTP = 780 ug/L multiplied by actual urine volume

Results corrected for creatinine by using an average concentration of 1500 mg for each worker per day.

example: (780 AM equiv/1409 mgs ttl crt) x 1500 mg = 830 AM eq.

Table V

Comparison of Exposure Estimates Based on DMTP Metabolites and Potential Dermal Exposure

Dermal Exposure (mg) Predicted from\a Urinary Metabolites	Observed from Shirts and Wipes	Ratio of observed to Predicted
5.8	12.5	2
3.4	19.7	6
2.6	17.4	7
13.0\b	36.6\c	3

\a Predicted dermal exposure = sum of 48 hour DMTP excretion x 10.

\b Sum of DMTP excretion for days 56, 57 and 58 x 10.

\c Sum of day 56 potential exposure and mean potential exposure from Table II for day 57.

Figure 1

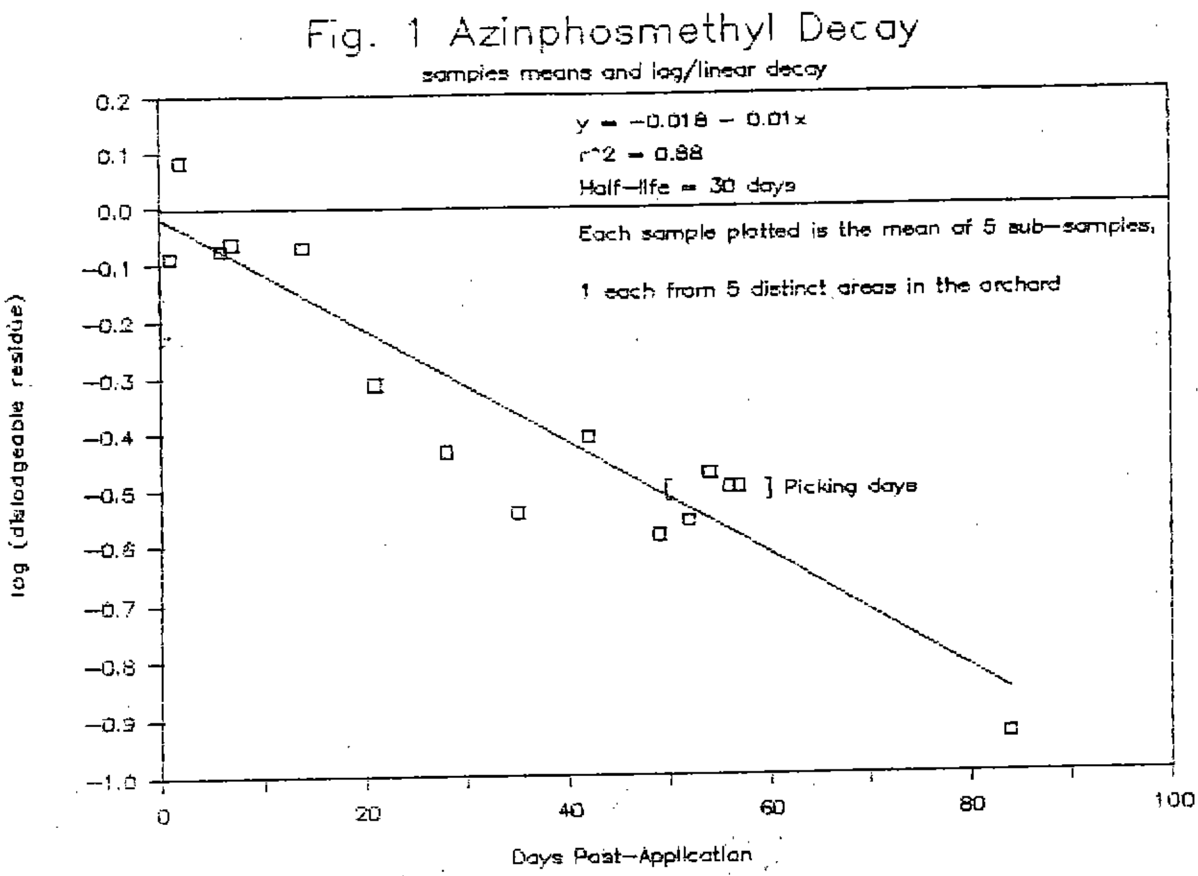
Fig. 1 Azinphosmethyl Decay
samples means and log/linear decay
y = -0.018 - 0.01x
r^2 = 0.88
Half-life = 30 days
Each sample plotted is the mean of 5 sub-samples,
1 each from 5 distinct areas in the orchard
] Picking days
log (dislodgeable residue)
Days Post-Application
0.2
0.1
0.0
-0.1
-0.2
-0.3
-0.4
-0.5
-0.6
-0.7
-0.8
-0.9
-1.0
0
20
40
60
80
100

Appendix 1

Potential Dermal Azinphos-Methyl Exposure to Nectarine Pickers (micrograms)

ID	Day	Longsleeve azm	Longsleeve oxon	Shirt total	Handwash azm	Handwash oxon	mL wash	Handwipes azm	Handwipes oxon	Total Hand exp.	Facewipes azm	Facewipes oxon	Total Face exp.	Total Potential Exposure
2	3	17000	507	17507	1110	60	465			1258	110	6	116	18881
2	5	15400	609	16009	3010	185	495			3435	142	6	148	19592
8	3	17100	890	17990	786	56	475			905	25	ND	25	18920
8	5	16400	1080	17480	1450	272	495			1852	65	10	74	19406
9	1	11650	747	12397	261	27	405	1720	127	2156	89	6	95	14648
10	3	11000	268	11268	1610	98	465			1836	58	4	62	13166
10	5	15200	756	15956	1651	164	485			1952	115	3	118	18026
11	3	19700	804	20504	1030	65	465			1177	66	3	69	21750
11	5	16400	821	17221	1730	266	510			2146	81	10	91	19458
13	3	5600	149	5749	797	51	480			912	22	1	24	6684
13	5	9000	302	9302	1570	236	493			1942	54	10	63	11307
16	3	15900	844	16744	1720	93	475			1949	48	ND	48	18740
16	5	13700	712	14412	1830	220	493			2204	124	12	136	16753
17	1	11480	941	12421	344	34	450	1290	85	1781	73	2	75	14277
17	3	19200	780	19980	662	38	455			753	55	3	58	20791
17	5	13900	864	14764	1050	161	495			1302	74	6	81	16147
23	3	12800	301	13101	371	32	485			433	48	3	52	13586
23	5	5610	134	5744	523	27	385			591	74	7	82	6417
24	1	8110	569	8679	309	43	470	1460	97	1936	104	9	113	10727
24	3	13800	687	14487	1300	67	480			1470	96	4	100	16057
24	5	20600	1250	21850	2190	337	483			2717	152	6	158	24725
25	3	12700	682	13382	1990	102	470			2249	79	3	82	15713
26	1	7220	456	7676	285	27	490	1590	112	2038	62	6	68	9782
26	3	18500	821	19321	1910	14	470			2069	122	5	127	21517
26	5	22400	1270	23670	1527	128	448			1780	146	5	151	25601
27	1	10640	826	11466	647	78	161	1180	72	2031	131	8	139	13636
27	3	18600	801	19401	850	74	445			993	65	4	69	20463
27	5	30000	1836	31836	1720	282	500			2153	192	7	199	34187
28	1	9780	337	10117	372	42	460	1270	93	1807	73	3	75	11999
30	3	18200	962	19162	907	68	455			1048	51	2	54	20263
30	5	16700	1058	17758	2400	409	510			3020	74	6	80	20858

Handwashes are calculated from 500 mL of sample solution.
Potential dermal exposure includes total shirt data and face and hand exposure.

Appendix 2

Baseline and Follow-up Results for Cholinesterase Activity

Worker ID	PLASMA B. L.	F. UP	Percent	RBC B. L.	F. UP	Percent
2	2655	2574	-3	8684	8785	+1
3*	2732	2652	-3	9534	9328	-2
4	2654	2456	-7	9128	9368	+3
5	3017	2935	-3	9111	9706	+6
6	3061	3134	+2	8363	8700	+4
9	3013	2937	-3	9744	9866	+1
11	2564	2929	+14	8020	9772	+1
12	3180	2978	-6	9198	8782	-5
14	2625	2729	+4	9108	1087	+1
15	3173	3451	+8	9570	9469	-1
17	3482	3493	0	11593	12207	+5
21	1834	1981	+7	10725	12035	+11
24	1991	2002	+1	8560	8761	+2
25	2496	2542	+2	9272	9393	+1
**	2501	2572	+3	10380	10140	-2
26	3100	3173	+2	9204	8612	-6
27	3296	3403	+3	9871	9995	+1
28	2965	3100	+4	10692	10432	-2
29	3030	3156	+4	11336	11249	-1

*crew leader
**survey person, not a harvester

Appendix 3

Twenty-Four Hour Urinary Metabolite Monitoring

ID	DAY	DMTP ug/L	Urine Volume Liters	Creatinine mgs/dl	Creatinine total	AM eq.	Corrected for Creatinine
1	3	610	0.25	330	825	340	618.31
1	4	229	0.65	222	1443	332	310.94
1	5	422	0.5	222	1110	470	571.58
1	6	1020	0.8	182	1456	1820	1687.2
1	7	111	0.6	228	1368	148	145.90
4	3	1277	0.6	218	1308	1709	1763.4
4	4	166	1.45	155	2248	537	322.41
4	5	593	1.1	60	660	1455	2976.8
4	6	824	0.8	122	976	1470	2033.3
4	7	267	0.5	176	880	297	455.85
5	3	133	0.5	179	895	148	223.01
5	4	89	1.9	78	1482	375	341.73
5	5	620	0.8	120	960	1106	1554.6
5	6	293	0.6	166	996	392	531.19
5	7	45	0.8	94	752	80	143.79
6	*3	40	0.2	133	266	18	90.541
6	4	86	0.75	184	1380	144	140.52
6	5	665	0.5	224	1120	741	893.74
6	6	587	0.6	212	1272	785	833.14
6	7	39	0.3	266	798	26	44.478
9	1	553	1.9	71	1349	2343	2344.3
9	2	153	2.1	66	1386	716	697.43
9	3	613	0.85	150	1275	1161	1229.4
9	4	135	0.85	74	629	256	549.61
9	5	970	1.2	148	1776	2595	1972.6
9	6	904	1.15	154	1771	2318	1767.2
9	7	259	1.45	100	1450	838	780.02
12	3	59	0.25	231	578	33	77.021
12	4	87	0.45	248	1116	87	105.12
12	5	76	0.3	182	546	51	125.54
12	6	392	0.4	244	976	350	483.53
12	7	142	1.2	64	768	381	669.36
14	3	182	0.45	235	1058	182	232.89
14	4	148	1.2	155	1860	395	286.87
14	5	180	0.9	142	1278	362	382.24
14	6	742	1.6	124	1984	2646	1800.4
14	7	156	1.15	154	1771	401	305.54
15	3	620	0.7	173	1211	967	1078.2
15	4	27	0.4	163	652	24	50.051
15	5	529	0.6	168	1008	707	947.41
15	6	303	1.3	58	754	879	1573.7
15	7	45	0.75	78	585	74	171.75
17	1	550	1.35	89	1202	1655	1859.4
17	2	141	1.8	58	1044	565	730.82
17	3	125	0.8	131	1048	224	288.18
17	4	204	1.1	82	902	501	749.32
18	3	22	0.3	265	795	15	25.447
18	4	236	0.55	316	1738	289	224.73
18	5	1575	0.75	172	1290	2634	2756.7
18	6	1660	1	158	1580	3702	3162.9
18	7	93	0.5	122	610	103	228.99
19	3	154	0.1	334	334	34	138.35
19	4	90	0.5	257	1285	100	105.19
19	5	656	0.7	174	1218	1024	1134.9
19	6	740	0.6	190	1140	990	1172.5
19	7	69	0.65	186	1209	100	111.35
20	3	183	0.25	220	550	102	250.18
20	5	1330	0.9	156	1404	2669	2566.6
20	6	673	1.1	68	748	1651	2979.9
20	7	152	0.85	188	1598	287	242.60
21	3	88	0.9	158	1422	177	168.43
21	4	165	1.45	92	1334	534	539.92
21	5	84	0.7	88	616	131	288.05
21	6	302	1.4	102	1428	944	892.22
21	*7	40	2.3	26	598	205	463.15
22	3	16	0.35	92	322	13	52.454

Appendix 3 (continued)

ID	DAY	DMTP ug/L	Urine Volume Liters	Creatinine mgs/dl	Creatinine total	AM eq.	Corrected for Creatinine
22	4	256	1	104	1040	570	739.59
22	5	244	0.6	92	552	326	796.80
22	6	1050	0.6	178	1068	1405	1775.8
22	7	140	2.1	66	1386	657	639.95
24	1	50	0.6	208	1248	67	72.657
24	2	22	0.3	243	729	15	27.751
24	3	404	0.8	271	2168	721	448.68
24	4	155	1.3	129	1677	449	361.72
26	1	160	0.6	271	1626	214	177.74
26	2	53	0.9	122	1098	106	130.53
26	3	64	0.7	138	966	99	138.52
26	4	110	0.9	76	684	221	436.52
27	1	197	0.5	234	1170	220	253.83
27	2	64	1.7	196	3332	242	98.148
27	3	492	0.45	224	1008	493	660.56
27	4	153	0.35	52	182	120	886.93
28	1	122	0.75	131	983	204	280.36
28	2	659	1	60	600	1470	3307.0
28	3	145	0.6	54	324	195	810.60
28	4	110	0.5	56	280	122	590.27
28	5	882	1.6	74	1184	3146	3586.5
29	*3	40	0.25	96	240	22	125.43
29	4	137	0.25	176	440	76	233.53
29	5	55	0.6	120	720	74	138.23
29	6	96	0.6	52	312	128	554.04
29	7	99	0.9	78	702	198	380.55

AM eq. azinphos-methyl equivalents = mol wt AM/mol wt DMTP (2.23*ugDMTP)
Correction = (AM equivalents * urine volume) * 1500 mgs creatinine/day
* Result reported is the DMTP detection limit

Appendix 4

Azinphosmethyl Dislodgeable Foliar Residues
Application through Harvest

NECTARINES, VAR. 227
RATE: 2#/acre
APPLICATION DATE: 5-25-88

Guthion (AZM) and guthion oxon residues reported in ug/cm^2

	INTERVAL																		
	4 HR	DAY 1	DAY 2	DAY 6	1 WK.	2 WEEKS		3 WEEKS		4 WEEKS		5 WEEKS		6 WEEKS		7 WEEKS		12 WEEKS	
	AZM	AZM	AZM	AZM	AZM	AZM	OXON	AZM	OXON	AZM	OXON	AZM	OXON	AZM	OXON	AZM	OXON	AZM	OXON
Mean a/	1.12	0.82	1.21	0.84	0.86	0.85	0.004	0.49	0.002 b/	0.37	0.007 b/	0.29	0.004	0.39	0.007	0.26	0.007	0.10	0.002
SD	0.24	0.07	0.17	0.09	0.05	0.15	0.001	0.06	---	0.08	---	0.05	0.002	0.06	0.002	0.10	0.002	0.05	0.001
Range																			
High	1.44	0.86	1.48	0.94	0.93	1.11	0.003	0.57	---	0.47	---	0.38	0.006	0.49	0.009	0.38	0.009	0.16	0.004
Low	0.84	0.70	1.06	0.71	0.80	0.72	0.005	0.43	---	0.29	---	0.21	0.003	0.33	0.005	0.14	0.004	0.05	0.001
Weekly Temperature °F																			
High	98	-	100	95	-	85		102		105		102		103		105		98	
Low	52		45	45		48		55		63		60		59		63		59	

a/ mean of five samples
b/ only one sample above detection limit
No oxon detected until day 14
Minimum detection limit = $0.003 ug/cm^2$